



# Synergistic effect and nanostructure engineering of three-dimensionally hollow mesoporous spherical $\text{Cu}_3\text{P}/\text{TiO}_2$ in aqueous/flexible Zn-air batteries

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## ABSTRACT

Designing materials with electron/mass transfer effectively improves catalytic activity by synergistic effects between different species. Herein, we report a high-temperature pyrolysis strategy to induce charge transfer of  $\text{Cu}_3\text{P}$  loaded  $\text{TiO}_2$  3D hollow mesoporous carbon nanospheres ( $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ ). Density functional theory (DFT) calculations disclose that synergistic between  $\text{Cu}_3\text{P}$  and  $\text{TiO}_2$  can optimize the adsorption of oxygen intermediates and endow fast reaction kinetics.  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  with hollow mesoporous structure can establish a favorable three-phase interface and shorten the electronic/mass transport path to accelerate reaction kinetics. Consequently,  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  indicated robust electrocatalytic activity in alkaline medium compared to single-component catalysts and benchmark Pt/C.  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  exhibits a greater power density of  $182.9 \text{ mW cm}^{-2}$  and excellent cyclability over 220 h than Pt/C +  $\text{RuO}_2$  in Zn-air battery. The flexible properties endow  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  with promising application prospects in wearable electronic devices. This work may provide an avenue to construct hollow-porous-structured catalysts with synergistic effects for renewable energy devices.

## 1. Introduction

Increasing environmental issues and fossil fuel depletion have inspired the advancement of sustainable and renewable energy conversion devices [1,2]. Fuel cells, metal-air batteries, and metal-ion batteries were promising next-generation energy devices due to their high efficiency and low  $\text{CO}_2$  footprints [3]. Thereinto, in response to the feature of portable and wearable flexible electronic devices [4], Zn-air batteries (ZAB) possesses the peculiarities of cost-effectiveness, extraordinary theoretical energy density ( $1086 \text{ Wh kg}^{-1}$ ), eco-friendliness, and intrinsic safety, which are demanded features of the next-generation sustainable flexible energy equipment [5–7]. Nevertheless, the bottleneck of ZAB's development stems from the sluggish kinetics of the oxygen reduction reaction (ORR) owing to its intricate multielectron transfer pathway occurring at the three-phase interface [8]. Although Pt-based materials were considered preeminent electrocatalysts, their extensive applications were inevitably plagued by high cost, scarcity, and insufficient durability [9,10].

Accordingly, putting more efforts into exploring active catalysts highly to vanquish the sluggish kinetics of ORR was critical for the pervasive application of ZAB.

A promising ORR electrocatalyst was generally dominated by the strong synergy between the metal and support and the porous structure in favor of electron/mass transport [11,12]. In this regard, porous carbon support can provide visible superiority because of its momentous conductivity and high specific surface area [13]. Particularly, pyridine N was considered the most favorable bonding mode for ORR in the existence of doped nitrogen [14]. Alternatively, transition metal oxides (TMO) have attracted interest as supports because of strong metal-support interactions (SMSI) between matrix and metal [15]. Previous studies have found that the strong SMSI of  $\text{TiO}_2$  originates from electronic interactions that accelerate the electron transfer [16,17]. Meanwhile, the rational combination of  $\text{TiO}_2$  and N-doped carbon materials can availably expand its electrical conductivity and thus enhance ORR performance [18]. Moreover, some reports indicated that the electronic structure of TMO supports was impacted by introducing

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transition metals [19–21]. The low conductivity and particles agglomeration features of transition metal phosphides (TMPs) with metalloid characteristics, such as  $\text{Cu}_3\text{P}$ , impede its application in electrocatalysis. However, charge transfer was induced by loading  $\text{Cu}_3\text{P}$  onto TMO support. Additionally, the encapsulation of carbonaceous material can resist agglomeration to enhance durability. The electrocatalyst was thus endowed with quick reaction kinetics. Combined with the above factors, we reported an innovative  $\text{Cu}_3\text{P}/\text{TiO}_2$  hybrid catalyst anchored on the 3D hollow mesoporous N-doped carbon nanospheres by high-temperature treatment. The electronic interaction between Ti and P species was induced by innovating  $\text{Cu}_3\text{P}$ . DFT calculations indicated that electron interaction between  $\text{Cu}_3\text{P}$  and  $\text{TiO}_2$  can stimulate charge transfer and reduce free energies of oxygen-containing intermediate, endowing catalyst fast ORR kinetics. Moreover, the N, C co-doped matrix helps to overcome the low conductivity of  $\text{TiO}_2$ . The unordinary hollow mesoporous structure constructs a suitable three-phase interface synchronously provides a larger specific surface area, contributing to reduce diffusion resistance and expose a high density of active sites. Consequently, the optimized catalyst displays excellent ORR activity in alkaline electrolyte, outperforming the benchmark Pt/C and mono-metallic materials. Notably, the  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ -based ZAB exhibits a high peak power density of  $182.9 \text{ mW cm}^{-2}$  and outstanding durability for 220 h, confirming its promising application in energy conversion devices.

## 2. Experimental procedures

### 2.1. Chemicals

Ammonium hydrogen difluoride (98 %), ethanol, ammonia solution (25–28 %), 1-Hexadecylamine (HAD, 90%), Copper (II) acetate monohydrate ( $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ ), analytic grade), melamine, red phosphorus (P) and Titanium isopropoxide (TIP, 95 %). Nafion solution (5 wt%) and Pt/C (20 wt%) were obtained from Alfa Aesar. The Milli-Q ultrapure water with a resistance of  $18.2 \text{ M}\Omega\text{-cm}$  was used in the experiment. All chemicals were used without further purification.

### 2.2. Synthesis of $\text{SiO}_2@\text{RF}$

The  $\text{SiO}_2@\text{RF}$  was prepared by stirring reaction under room temperature according to our previous work [22].

### 2.3. Synthesis of $\text{TiO}_2@\text{NC}$

The  $\text{TiO}_2 @\text{NC}$  was prepared according to the reported work with slightly modification [23]. In a typical procedure, 360 mg  $\text{SiO}_2@\text{RF}$  and 320 mg HAD was dissolved in a mixture of 0.8 mL of ammonia solution and 31.0 mL of ethanol. After ultrasonic treatment for 30 min, 0.4 mL of TIP was fleetly dropped into the above solution with successive agitating for 2 h at room temperature. The precipitates were centrifuged and washed with ethanol several times to eliminate superfluous organic species and dried in oven  $60^\circ\text{C}$ . Subsequently, the obtained product was uniformly ground with melamine (mass ratio=1:5) and annealed at  $700^\circ\text{C}$  for 3 h under  $\text{N}_2$  atmosphere with a heating rate of  $5^\circ\text{C}/\text{min}$ . The  $\text{SiO}_2$  core was etched by 1 M ammonium hydrogen difluoride solution for 12 h to obtain  $\text{TiO}_2@\text{NC}$ .

### 2.4. Synthesis of $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$

A certain amount of  $\text{TiO}_2@\text{NC}$ , 50 mg  $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$  and x mg P (x = 50, 100, 200) were ground uniformly and calcined at  $T^\circ\text{C}$  ( $T = 800, 900, 1000$ ) for 2 h under  $\text{N}_2$  atmosphere. the  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  refers to that product obtained at a temperature of  $900^\circ\text{C}$  and P of 100 mg unless stated otherwise.

As a control, the  $\text{Cu}_3\text{P}/\text{C}$  was prepared by using the same protocol except that carbon black was regarded as the support.

## 3. Results and discussion

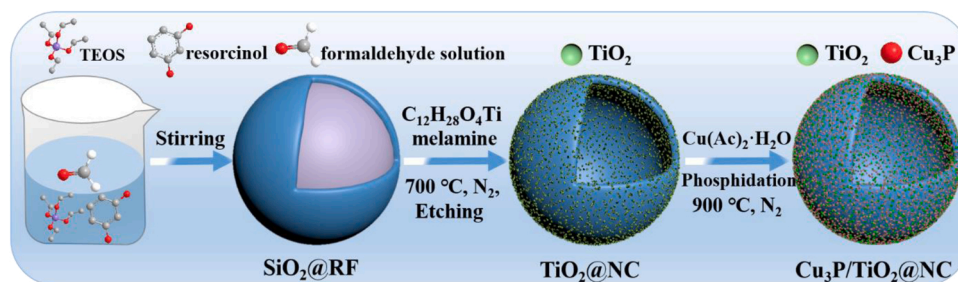
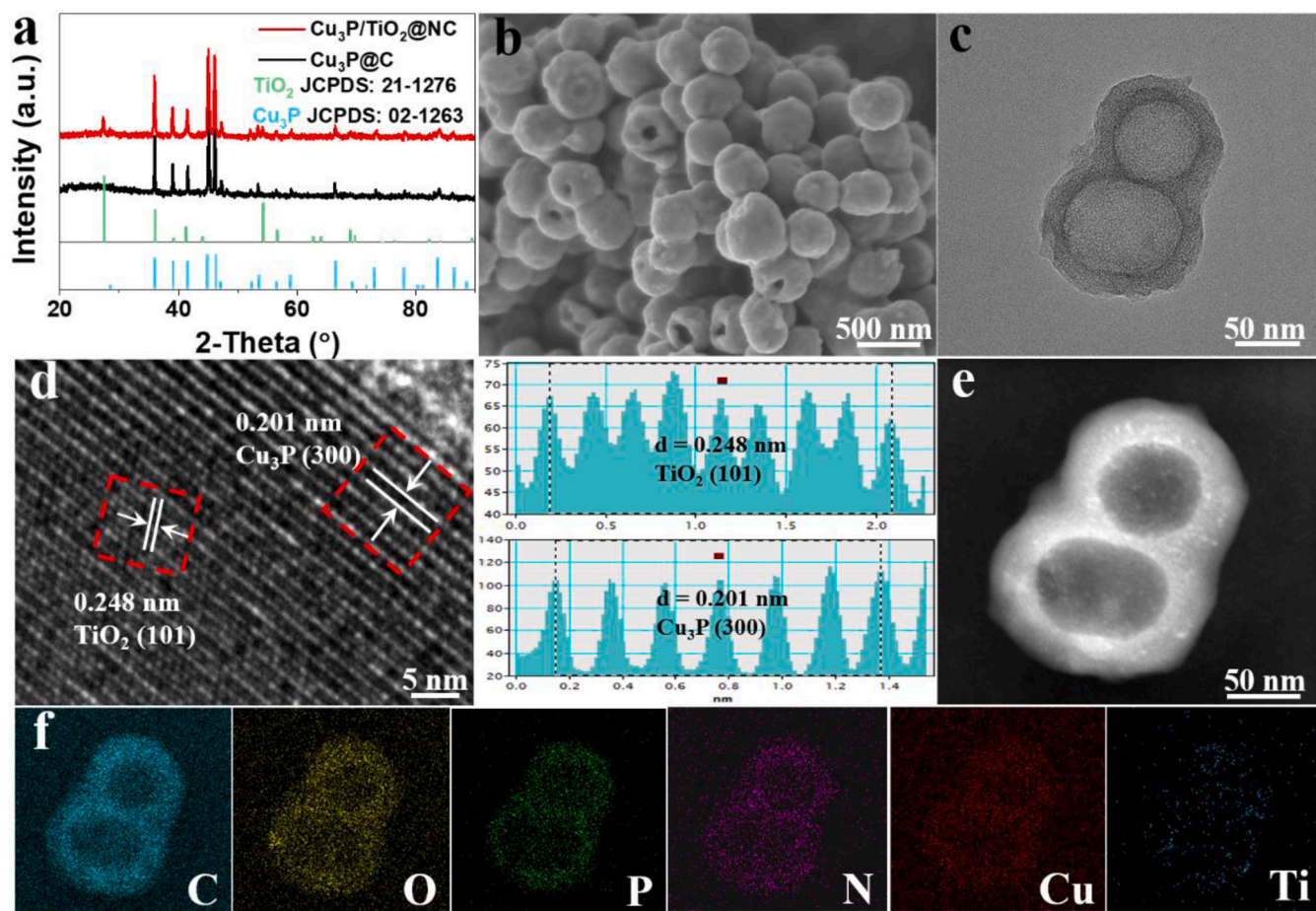
### 3.1. Synthesis and characterization of catalysts

As depicted in Scheme 1, the  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  was obtained by a facile high-temperature phosphating process to load the  $\text{Cu}_3\text{P}$  species on the  $\text{TiO}_2@\text{NC}$  hollow nanospheres. Specifically,  $\text{SiO}_2@\text{RF}$  nanospheres were synthesized via a phenolic reaction to coat carbonaceous substances on the surface of  $\text{SiO}_2$ . After that, HDA and  $\text{SiO}_2@\text{RF}$  nanospheres were uniformly dispersed in a mixed solution so that HDA surfactants was segregated to the surface of the nanospheres. TIP was subsequently added to the above solution under stirring. The amino groups of HDA interact with the TIP hydrolysate to form a composite material coated with the nanospheres [24]. The X-ray diffraction (XRD) pattern of  $\text{TiO}_2@\text{NC}$  was obtained by removing the  $\text{SiO}_2$  core, and it somewhat displays the characteristic diffraction peaks of monoclinic  $\text{TiO}_2$  (JCPDS: 46–1238 and 48–1278), confirming the  $\text{TiO}_2$  loading onto the template (Fig. S1) [25]. Transmission electron microscope (TEM) and scanning electron microscope (SEM) indicated that  $\text{TiO}_2@\text{NC}$  exhibits a hollow structure (Figs. S2a–b). Furthermore, the homogeneous dispersion of C, N, O and Ti on the entire nanosphere was confirmed by elemental mappings (Fig. S2c). Afterwards, Cu ions were loaded on the  $\text{TiO}_2@\text{NC}$  nanospheres during the high-temperature phosphating. The Cu ions amount was up to 35.86 wt%, as corroborated by inductively coupled plasma mass spectroscopy (ICP-MS) (Table S1). Of note, red P was considered an environment-friendly phosphorus source owing to not engender toxic gases at high-temperature process.

The crystal phases of the resultant catalysts were authenticated by XRD patterns (Fig. 1a). The primary peaks were matched well with hexagonal  $\text{Cu}_3\text{P}$  (JCPDS: 02–1263) and tetragonal  $\text{TiO}_2$  (JCPDS: 21–1276) [22,25], indicating the formation of  $\text{Cu}_3\text{P}$  with high phase-purity and crystallinity in the  $\text{TiO}_2@\text{NC}$  support. Notably, the crystal structure of  $\text{TiO}_2$  transforms from monoclinic to tetragonal crystal phase owing to the temperature increment [26]. The morphology and microstructure of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  was revealed by SEM and TEM. The  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  took on a hollow structure similar to  $\text{TiO}_2@\text{NC}$ , confirming that the support structure was not destroyed after loading  $\text{Cu}_3\text{P}$  (Fig. 1b–c and Fig. S3). Generally, the hollow structure was promising to expedite the mass and electron transfer during the reaction [27,28]. The high-resolution TEM (HR-TEM) image and the corresponding lattice spacing profiles were presented in Fig. 1d. The lattice strips with spacings of 0.248 and 0.201 nm in the red region can be retrieved to the (300) plane of  $\text{Cu}_3\text{P}$  and the (101) plane of  $\text{TiO}_2$ , respectively [29]. The subtle distortion region can be sharply observed in the HR-TEM image of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ , which was attributed to the contact between the  $\text{Cu}_3\text{P}$  and  $\text{TiO}_2$  particles (Fig. S4) [30]. Simultaneously, the hollow structure of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  was further unveiled by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in Fig. 1e. The corresponding element mappings elucidated the uniform distribution of C, O, P, N, Cu and Ti elements in the nanosphere (Fig. 1f). Besides, ICP-MS and element mapping confirmed that the weak lattice fringes of  $\text{TiO}_2$  in the HR-TEM image was attributed to the low content of Ti in  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ . As expected, the above results confirmed that  $\text{Cu}_3\text{P}$  was successfully incorporated into the  $\text{TiO}_2@\text{NC}$  support.

The Raman spectra of all catalysts were plotted in Fig. 2a. Generally, D- and G-band reflect the disorder or edge defects and graphitization degree of carbon species, respectively [31,32]. The intensity ratio ( $I_D/I_G$ ) of the D- and G-band of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  (1.39) was higher than that of  $\text{Cu}_3\text{P}/\text{C}$  (1.28) and  $\text{TiO}_2@\text{NC}$  (1.10), confirming that the catalyst harvests more edge defects after loading  $\text{Cu}_3\text{P}$  [33,34]. As a result, it is conducive to improve the electrocatalytic activity of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ .

The  $\text{N}_2$  adsorption/desorption isotherm manifests the IV-type curves with palpable hysteresis loop that confirmed the mesoporosity of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  nanospheres [35]. The generation of mesopores may be attributed to the elimination of  $\text{SiO}_2$  core. Meanwhile, the

Scheme 1. Schematic diagram of the synthesis of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ .Fig. 1. (a) XRD patterns of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  and  $\text{Cu}_3\text{P}@\text{C}$ . (b) SEM, (c) TEM, (d) HR-TEM and the corresponding lattice spacing profiles of the dotted line regions, (e) HAADF-STEM images and (f) elemental mappings of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ .

Brunauer-Emmett-Teller (BET) surface area of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  was calculated to be  $196.3 \text{ m}^2 \text{ g}^{-1}$  (Fig. 2b), which was conducive to increase the attainability of active sites [36]. The active catalyst nanoparticles were located on the inner and outer surfaces of shell owing to unique hollow mesoporous structure. Moreover, the mesoporous network connecting the interior and exterior provide channels for reactant molecules diffusion into the active site. The mesoporous structure was further affirmed by pore-size distribution ( $\approx 5.3 \text{ nm}$ , inset in Fig. 2b), which favored adsorption of  $\text{O}_2$  molecule and transport of electrons and mass at the three-phase interface and exhibited enhanced ORR activity [34,37]. As depicted in Fig. 2c and S5,  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  ( $121.1^\circ$ ) has a smaller contact angle compared to  $\text{Cu}_3\text{P}/\text{C}$  ( $129.3^\circ$ ) and  $\text{TiO}_2@\text{NC}$  ( $131.8^\circ$ ), elucidating that  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  possesses higher hydrophilicity. Hydrophilicity can be explained according to the equation:  $h = 2\sigma\cos\theta/(\rho g r)$  [38]. The liquid height ( $h$ ) is proportional to the

capillary radius ( $r$ ). Therefore, the  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  with hollow mesoporous structure can provide a more potent capillary force to facilitate electrolyte diffuse, promoting the contact between active sites with reactants and accelerating ORR kinetics [39,40].

The surface composition and chemical environment of catalysts were further investigated by X-ray photoelectron spectroscopy (XPS). The survey spectra manifest the co-existence of Cu, Ti, C, O, N and P elements in the as-prepared materials, which was coincident with mapping analysis (Fig. S6a). As depicted in Figs. S6b-d, the high-resolution C 1s spectra of as-prepared catalysts were deconvoluted into four peaks as C=C (284.0 eV), C-C (284.8 eV), C-O/C-N (285.8 eV), O-C=O (288.0 eV) [41]. Pyridinic-N (397.8 eV), pyrrolic-N (399.2 eV) and graphitic-N (400.6 eV) were displayed in the high-resolution N 1s spectra (Figs. S6e-f) [42]. Among them, pyridinic-N and graphitic-N can modulate the charge redistribution to enhance the ORR catalytic activity



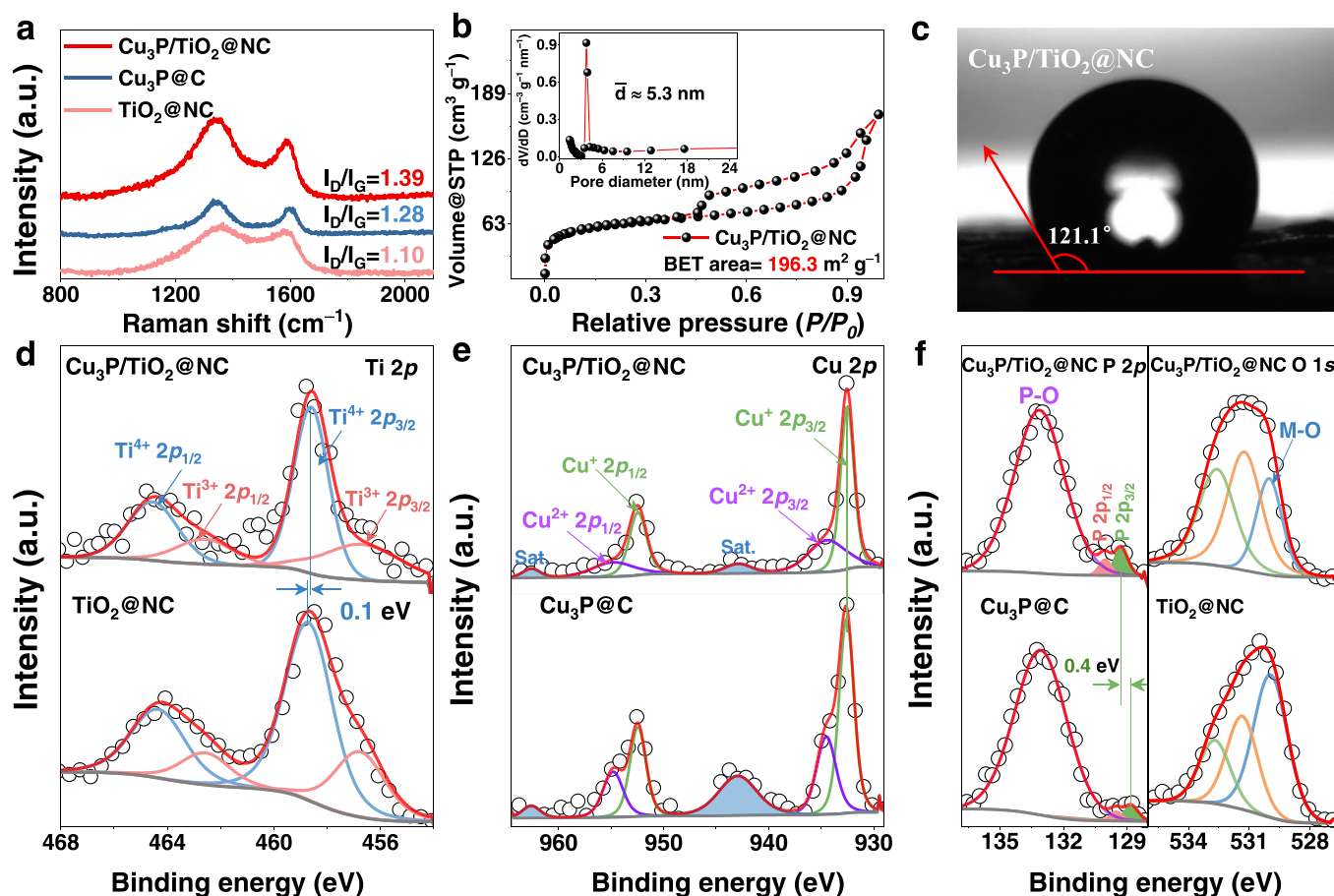


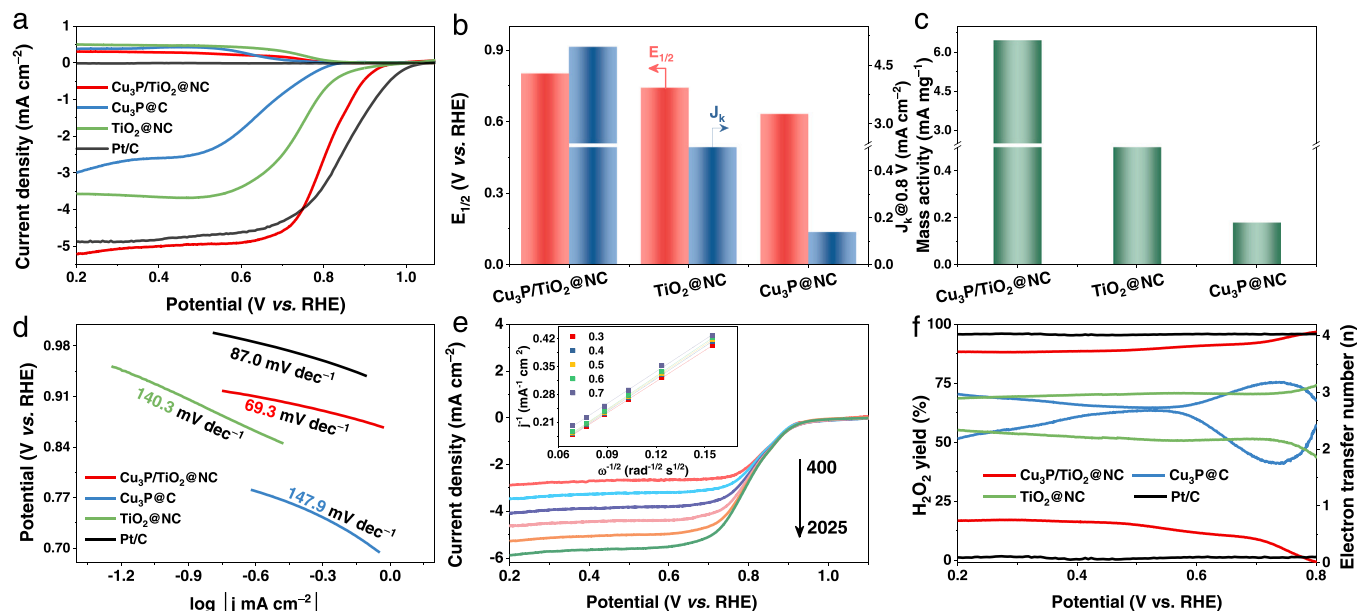
Fig. 2. (a) Raman spectra of the different catalysts. (b)  $\text{N}_2$  adsorption/desorption isotherms and corresponding pore size distribution for  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  (inset). (c) Bubble contact angle image of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ . High-resolution XPS spectra of (d) Ti 2p, (e) Cu 2p, and (f) P 2p and O 1s regions in  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ ,  $\text{Cu}_3\text{P}@\text{C}$ , and  $\text{TiO}_2@\text{NC}$ , respectively.

[43]. The Ti 2p spectrum of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  indicates two peaks at 458.6 and 464.5 eV were assigned to  $2p_{3/2}$  and  $2p_{1/2}$  of  $\text{Ti}^{4+}$  in  $\text{TiO}_2$  [44]. The doublet peaks of  $\text{Ti}^{3+}$  appear 456.7 and 462.6 eV, indicating the partial reduction of  $\text{Ti}^{4+}$  by carbon at high temperature [45]. The binding energies of  $\text{Ti}^{4+}$  are 0.1 eV lower than that of  $\text{TiO}_2@\text{NC}$  (Fig. 2d). Furthermore, in the Cu 2p region of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  and  $\text{TiO}_2@\text{NC}$  (Fig. 2e), the peaks at 932.5 and 952.4 eV were indexed to the Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  of  $\text{Cu}^+$  in  $\text{Cu}_3\text{P}$ , respectively. The binding energies at 934.5 and 954.8 eV were assigned to  $\text{Cu}^{2+}$ , resulting from surface oxidation upon exposure to the air. Furthermore, the peaks centered at 942.9 and 962.6 eV contributed to satellite peaks [46]. The presence of  $\text{Cu}^+$  was further corroborated by auger electron spectroscopy (AES) (Fig. S7). The P 2p spectrum was fitted into three peaks at 129.3, 130.0 and 133.1 eV corresponding to  $2p_{3/2}$  and  $2p_{1/2}$  of Cu-P and P-O bonds [47]. The presence of P-O bonds was attributed to the surface oxidation of phosphide. Meanwhile, the O 1s spectra emerge three palpable peaks at 530.0, 531.3 and 532.6 eV can be attributed M-O, C-O and adsorbed OH groups, respectively (Fig. 2f) [48,49]. Interestingly, the binding energies of Cu-P display positive shifted by 0.4 eV compared with  $\text{Cu}_3\text{P}@\text{C}$ . The shift of  $\text{Ti}^{4+}$  and Cu-P in the binding energy demonstrates the charge transfer from P to Ti species, revealing that the introduction of  $\text{Cu}_3\text{P}$  promotes strong electronic interactions [50]. Notably, the interaction, engendered by charge redistribution, give rise to faster charge/mass transfer and enhance ORR activity [51]. As expected, XPS analysis verified that the successful preparation of  $\text{Cu}_3\text{P}$  and  $\text{TiO}_2$ , which is identical with the XRD and HR-TEM results.

### 3.2. Electrocatalytic ORR activity of materials

The electrocatalytic ORR performance of as-prepared materials was estimated in 0.1 M KOH solution. The optimal catalyst, noted as  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ , was obtained when the mass ratio of red P to precursor was 2/1 and the calcination temperature was  $900^\circ\text{C}$  during a series of optimization (Figs. S8 and S9). As displayed in Fig. S10, the cyclic voltammetry (CV) curves of all catalysts exhibited distinct reduction peaks in  $\text{O}_2$ -saturated electrolytes compared to  $\text{N}_2$ -saturated ones, confirming the selectivity of the catalysts for oxygen reduction. Furthermore, the anodic/cathode peaks at 0.90 and 0.61 V were assigned to the redox reactions of Cu species [52]. Moreover,  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ ,  $\text{Cu}_3\text{P}@\text{C}$  and  $\text{TiO}_2@\text{NC}$  exhibited poor OER performance (Fig. S11).

Linear sweep voltammetry (LSV) curves of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  manifest an onset potential ( $E_{\text{onset}}$ ) of 0.95 V and a half-wave potential ( $E_{1/2}$ ) of 0.80 V, which were substantially superior to those of  $\text{Cu}_3\text{P}@\text{C}$  (0.80 V, 0.63 V),  $\text{TiO}_2@\text{NC}$  (0.90 V, 0.74 V) and most recently reported transition metal-based electrocatalysts (Table S2), whereas slightly lower than Pt/C (1.01 V, 0.85 V) (Fig. 3a). The above results illustrated that  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  bears favorable ORR activity, which attributed to the strong electronic interaction induced by introducing  $\text{Cu}_3\text{P}$  and the hollow mesoporous structure critical to expose more active sites. Notably,  $\text{TiO}_2$  was regarded as the main active center.  $\text{Cu}_3\text{P}$  plays an auxiliary role. Moreover, the kinetic density ( $J_k$ ) of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  is as high as  $4.95 \text{ mA cm}^{-2}$  at 0.8 V in contrast to  $\text{Cu}_3\text{P}@\text{C}$  ( $0.14 \text{ mA cm}^{-2}$ ) and  $\text{TiO}_2@\text{NC}$  ( $0.95 \text{ mA cm}^{-2}$ ), explicating that  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  possessed faster kinetics (Fig. 3b) [53]. The mass activity of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  was up to  $6.43 \text{ mA mg}^{-1}$  at 0.8 V, which was 35.7 and 5.2 times higher than that



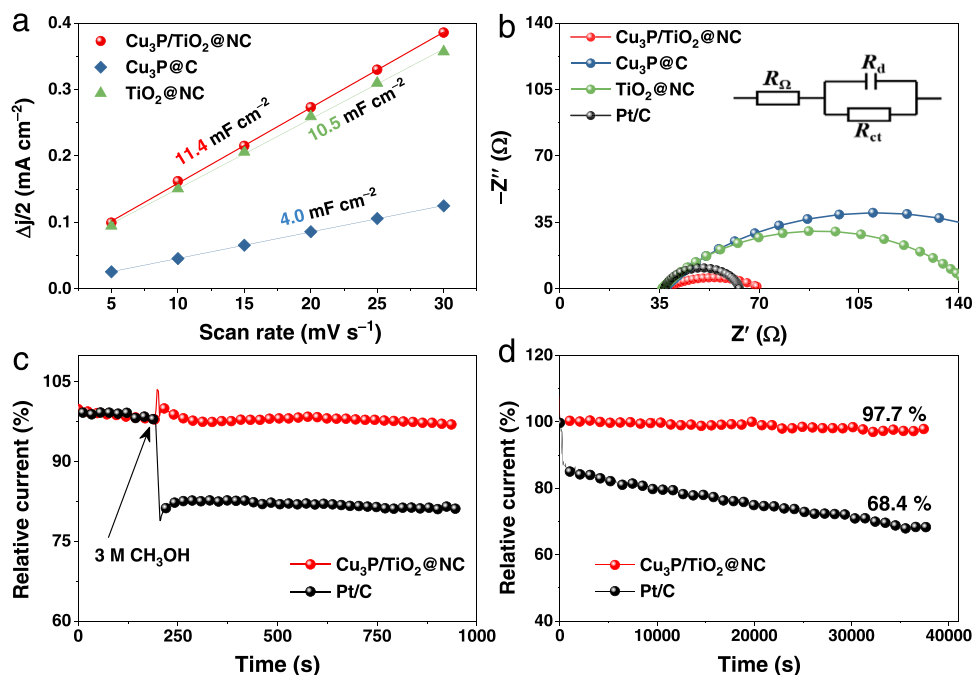
**Fig. 3.** Electrocatalytic ORR performances of the catalysts in 0.1 M KOH solutions. (a) LSV curves, (b) summary of the corresponding  $E_{1/2}$  and  $J_k$  ( $E = 0.8$  V) values, and (c) mass activity ( $E = 0.8$  V) of the as-prepared catalysts and Pt/C. (d) Tafel plots. (e) Polarization curves of Cu<sub>3</sub>P/TiO<sub>2</sub>@NC at various rotating speeds from 400 to 2025 rpm and the corresponding K-L plots (inset). (f) H<sub>2</sub>O<sub>2</sub> yield (%) and electron transfer number (n) from various catalysts.

of Cu<sub>3</sub>P@C (0.18 mA mg<sup>-1</sup>) and TiO<sub>2</sub>@NC (1.23 mA mg<sup>-1</sup>), respectively, certifying that its great potential for practical applications (Fig. 3c) [54]. As shown in Fig. 3d, Cu<sub>3</sub>P/TiO<sub>2</sub>@NC exhibited the lowest Tafel slope value of 69.3 mV dec<sup>-1</sup> being beyond Cu<sub>3</sub>P@C (147.9 mV dec<sup>-1</sup>), TiO<sub>2</sub>@NC (140.3 mV dec<sup>-1</sup>) and benchmark Pt/C (87.0 mV dec<sup>-1</sup>), suggesting more advantageous kinetics during ORR.

The reaction mechanism of Cu<sub>3</sub>P/TiO<sub>2</sub>@NC was elucidated by rotating disk electrode (RDE) technique. As illustrated in Fig. 3e, the Koutecky-Levich (K-L) plot with good linearity was obtained by recording LSV curves at various rotation speeds. This was accordance with the first-order reaction kinetics of ORR [55]. The electron transfer

number (n) was calculated to be about 3.5 according to the K-L equation, signifying that ORR process follows a four-electron transfer pathway. The rotating ring-disk electrode (RRDE) technique was executed to further interrogate the reaction mechanism. The value of n was evaluated to be ~3.7 (Fig. 3f), which is consistent with the RDE analysis. Simultaneously, the H<sub>2</sub>O<sub>2</sub> yield of Cu<sub>3</sub>P/TiO<sub>2</sub>@NC (< 20 %) visibly lower than that of Cu<sub>3</sub>P@C and TiO<sub>2</sub>@NC, exemplifying that the electronic interaction of TiO<sub>2</sub> induced by Cu<sub>3</sub>P has an indispensable effect on the selectivity of product.

To further probe the intrinsic activity of electrocatalyst. The electrochemically active surface area (ECSA) was discussed by calculating



**Fig. 4.** (a)  $C_{dl}$  values (b) Nyquist plots of the impedance for the catalysts and the corresponding equivalent circuit (inset). (c) Methanol tolerance tests and (d) Chronoamperometric response of Cu<sub>3</sub>P/TiO<sub>2</sub>@NC and Pt/C.

the value of the electric double-layer capacitance ( $C_{dl}$ ) [56].  $C_{dl}$  was obtained based on CV curves at various scan rates from 5 to 30  $\text{mV s}^{-1}$  (Fig. S12). The  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  arises a  $C_{dl}$  value of 11.4  $\text{mF cm}^{-2}$ , outperforming those of  $\text{Cu}_3\text{P}/\text{C}$  (4.0  $\text{mF cm}^{-2}$ ) and  $\text{TiO}_2@\text{NC}$  (10.5  $\text{mF cm}^{-2}$ ), meaning that  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  can expose more active sites to contact with reactants and boost ORR performance (Fig. 4a). The above results can be attributed to the large specific surface area of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  with a hollow mesoporous structure. Electrochemical impedance spectroscopy (EIS) certified that  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  possesses comparatively small charge transfer resistance (Fig. 4b), attesting the heightened ORR kinetics by introducing  $\text{Cu}_3\text{P}$ . The stability and methanol tolerance were essential parameters for evaluating catalysts. As presented in Fig. 4c, the current of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  undergoes a tiny drop compared to Pt/C after the addition of methanol at approximately 200 s. In addition, the robust stability of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  was testified by current retention of 97.7% after the chronoamperometric response of 40000 s (Fig. 4d). The above results signify that  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  possesses admirable methanol tolerance and stability than that of Pt/C, meaning it has potential practical application prospects in direct methanol fuel cells and metal-air battery.

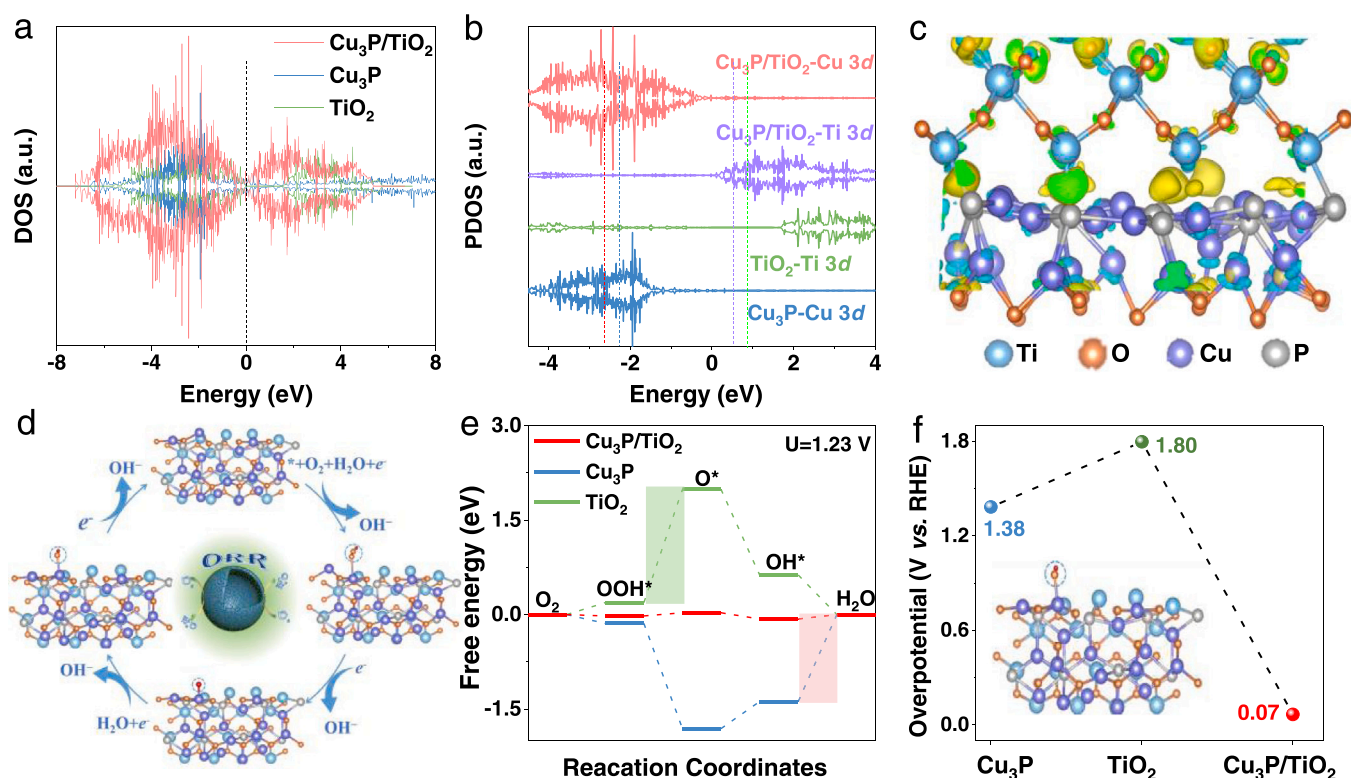
### 3.3. DFT calculation

DFT calculations were performed to elucidate the influence of leading into  $\text{Cu}_3\text{P}$  in the electronic structure and ORR activity of  $\text{TiO}_2$ . The optimized structure models of  $\text{Cu}_3\text{P}/\text{TiO}_2$ ,  $\text{Cu}_3\text{P}$ , and  $\text{TiO}_2$  were shown in Fig. S13. The calculated density of states (DOS) and partial density of states (PDOS) of different models were depicted in Fig. 5a and b, respectively. The higher DOS around the Fermi level of  $\text{Cu}_3\text{P}/\text{TiO}_2$  than that of  $\text{TiO}_2$  due to the introduction of  $\text{Cu}_3\text{P}$ , which impacted the electronic structures of  $\text{TiO}_2$ . Consequently,  $\text{Cu}_3\text{P}/\text{TiO}_2$  composites enhance electron transport properties and facilitate adsorption/desorption of oxygen-containing intermediates, thereby improving the

conductivity and reducing the reaction energy barriers [57]. As a complement, PODS results illustrated that the  $d$ -band center values of Cu and Ti ( $-2.64$  and  $0.05$  eV) in  $\text{Cu}_3\text{P}/\text{TiO}_2$  were more negative relative to those of  $\text{Cu}_3\text{P}$  ( $-2.29$  eV) and  $\text{TiO}_2$  ( $0.87$  eV). The lower  $d$ -band center of Cu and Ti in  $\text{Cu}_3\text{P}/\text{TiO}_2$  was promising to weaken the adsorption of oxygen intermediates, hence accelerating ORR reaction kinetics [58]. In addition, Fig. 5c indicated that the electrons were accumulated in the edge of  $\text{Cu}_3\text{P}$ , whereas the one was depleted around  $\text{TiO}_2$ . The result suggests the existence of charge synergistic between  $\text{Cu}_3\text{P}$  and  $\text{TiO}_2$ , which was consistent with the XPS analysis. The Gibbs free energy was a key parameter for annotating the origin of electrocatalytic activity. The corresponding free energy variations of intermediates were calculated based on the stable adsorption configurations (Fig. 5d). As indicated in Fig. S14 and Table S3, all elementary steps were exothermic processes in  $\text{Cu}_3\text{P}/\text{TiO}_2$  and  $\text{Cu}_3\text{P}$ . In contrast, the formation of  $\text{O}^*$  was endothermic in  $\text{TiO}_2$  at an equilibrium potential of 0 V. Consequently, at  $U = 1.23$  V, the transition from  $\text{OOH}^*$  to  $\text{O}_2^*$  was rate-determining steps (RDS) in  $\text{TiO}_2$  (Fig. 5e). Differently, the  $\text{OH}^*$  intermediate desorption was changed to RDS when the introduction of  $\text{Cu}_3\text{P}$ . Simultaneously,  $\text{OH}^*$  desorption free energy in  $\text{Cu}_3\text{P}/\text{TiO}_2$  ( $0.07$  eV) was lower than that of  $\text{Cu}_3\text{P}$  ( $1.38$  eV), which was propitious for the desorption behavior of  $\text{OH}^*$  in the composites. Excitingly, the overpotential of  $\text{Cu}_3\text{P}/\text{TiO}_2$  was distinctly lower than those of  $\text{Cu}_3\text{P}$  and  $\text{TiO}_2$  (Fig. 5f). The above results indicated that the strong interaction between  $\text{Cu}_3\text{P}$  and  $\text{TiO}_2$  was conducive to optimizing adsorption of oxygen intermediates and facilitate electron transfer, thus  $\text{Cu}_3\text{P}/\text{TiO}_2$  exhibited the best ORR activity, which was in agreement with the experimental results.

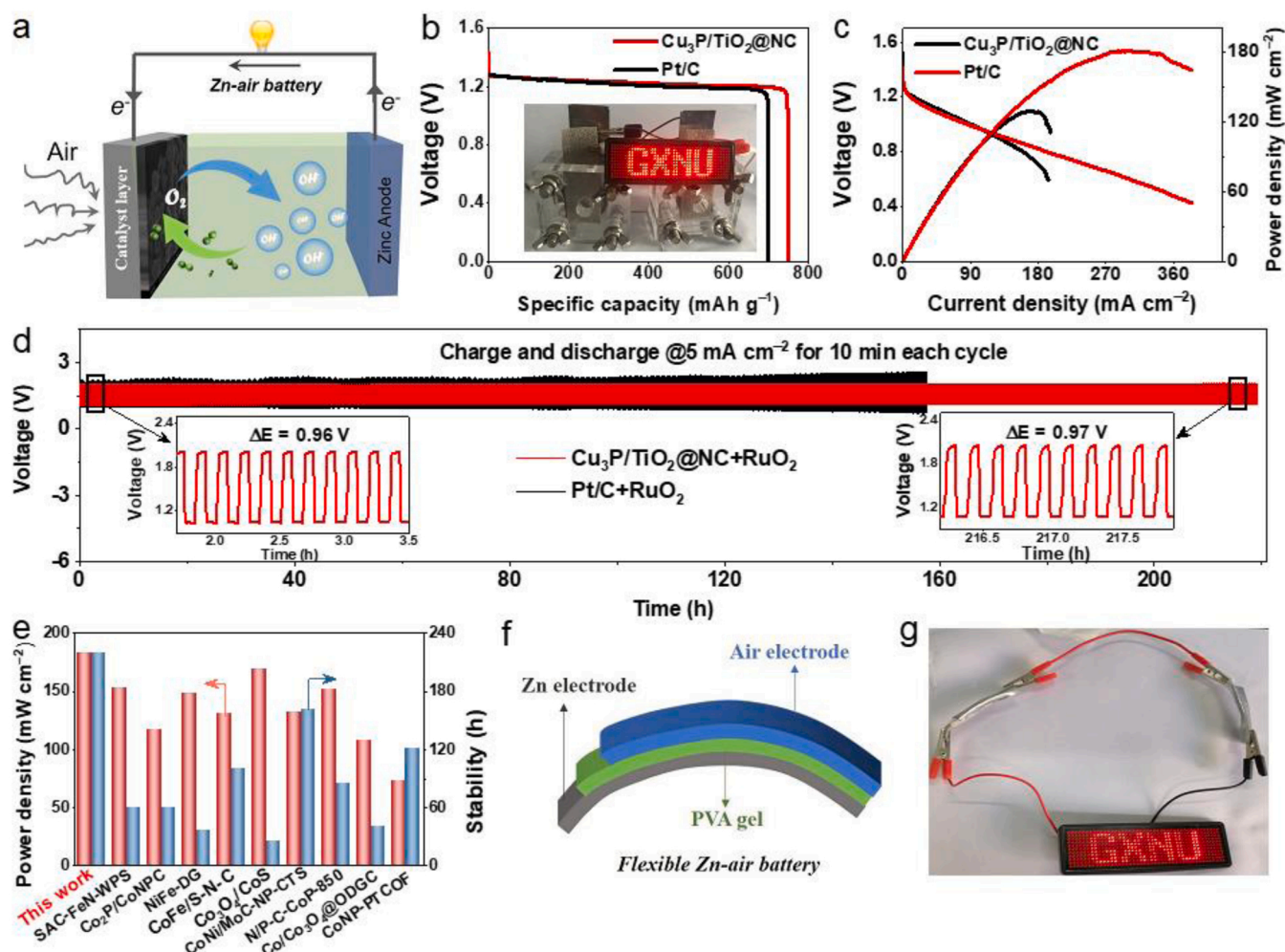
### 3.4. Performance of Zn-air battery

The Zn-air battery (ZAB) was constructed by applying  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  as air cathode to appraise its feasibility in practice energy storage-conversion equipment (Fig. 6a). Fig. S15a shows that  $\text{Cu}_3\text{P}/$



**Fig. 5.** (a) DOS, (b) PDOS of Ti 3d and Cu 3d orbitals of different models. (c) The charge density differences of  $\text{Cu}_3\text{P}/\text{TiO}_2$  model. Yellow and green region depict electron accumulation and depletion, respectively. (d) The reaction mechanism of ORR on  $\text{Cu}_3\text{P}/\text{TiO}_2$  model in 0.1 M KOH electrolyte. (e) Free energy diagram of ORR at an equilibrium potential of 1.23 V, and (f) corresponding overpotential (inset: RDS of  $\text{Cu}_3\text{P}/\text{TiO}_2$  configuration) for  $\text{Cu}_3\text{P}/\text{TiO}_2$ ,  $\text{Cu}_3\text{P}$ , and  $\text{TiO}_2$ .





**Fig. 6.** Application of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  in Zn-air batteries. (a) Schematic configuration of the liquid ZAB. (b) Specific capacity plots and digital image of LED panel lit by two ZABs in series (inset). (c) Discharge curves and the corresponding power densities of the catalysts. (d) Long-term cycling stability of liquid ZAB at  $5.0 \text{ mA cm}^{-2}$ . (e) Power density and stability contrast of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  with currently reported transition metal catalysts. (f) Schematic of the all-solid-state flexible ZAB. (g) Photograph of LED panel powered by two solid-state ZABs in series.

$\text{TiO}_2@\text{NC}$ -based ZAB achieved an open circuit voltage (OCV) of 1.30 V, reasonably lower than that of Pt/C (1.47 V). Additionally, Fig. 6b indicates that ZAB based on  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  delivers a specific capacity ( $747.3 \text{ mAh g}_{\text{Zn}}^{-1}$ , 91.1% utilization of the theoretical capacity) larger than that of Pt/C ( $700.0 \text{ mAh g}_{\text{Zn}}^{-1}$ , 85.4 %) [59]. As a practical illustration, the LED plate with a voltage of  $\sim 3 \text{ V}$  can be lit by connecting two ZABs in series (inset in Fig. 6b). Fig. 6c shows the polarization curves of ZAB, the peak power density of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  reaches  $182.9 \text{ mW cm}^{-2}$ , which is evidently higher than that of Pt/C ( $129.4 \text{ mW cm}^{-2}$ ). Furthermore, the discharge curves of the  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$ -based ZAB at various current densities declared that the voltage retention was 99% when the current density was recovered to  $2 \text{ mA cm}^{-2}$ , acknowledging its good rate capability (Fig. S15b).

The durability of ZAB was evaluated by charge-discharge cycling testing at a galvanostatic current of  $5 \text{ mA cm}^{-2}$ . The  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}+\text{RuO}_2$ -based ZAB exhibits superior stability with almost negligible attenuation of the discharge-charge voltage gap after 220 h of continuous operation. In contrast, the Pt/C+ $\text{RuO}_2$ -based ZAB exhibits a conspicuous decay after 160 h, which further elaborates the distinguished ORR stability of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  (Fig. 6d). Fig. 6e indicates that the power density and stability of ZAB assembled with  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  as an air cathode is also comparable among recently reported most catalysts. The schematic diagram and photographs of the flexible ZAB were depicted in Fig. 6f and Fig. S16. Interestingly, two flexible ZABs

connected in series can successfully power a LED plate (Fig. 6g). As expected,  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  possesses promising applications in energy conversion devices.

Taken together,  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  exhibits robust ORR activity and stability compared to  $\text{Cu}_3\text{P}/\text{C}$ ,  $\text{TiO}_2@\text{NC}$ , and Pt/C due to its distinctive structural superiority: (i) The hollow mesoporous structure of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  provide a good three-phase contact interface and shortens ion transport paths to expedite ORR kinetics [60]. (ii) The large specific surface area of  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  with hollow mesoporous structure can expose more active sites. (iii) The strong synergistic effect between  $\text{Cu}_3\text{P}$  and  $\text{TiO}_2$  species can modulate electronic structure resulting in faster electronic/mass transport and fast reaction kinetics [61]. Furthermore, the hollow structure with larger empty space was favorable for storing charges, which enables  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  to exhibit superb cyclical stability in practical applications [51].

#### 4. Conclusions

To summarize, we have affirmed a strategy to induce charge transfer feature of composites by doping  $\text{Cu}_3\text{P}$  at high temperature. The optimized  $\text{Cu}_3\text{P}/\text{TiO}_2@\text{NC}$  catalyst exhibits excellent ORR activity with a half-wave potential of 0.80 V, outperforming the benchmark Pt/C and recently reported transition metal-based catalysts. XPS and DFT calculation indicated that the superior ORR performance originates from the

strong synergistic effect between  $\text{Cu}_3\text{P}$  and  $\text{TiO}_2$  species. Furthermore, BET and contact angle tests confirmed that a high specific surface area of  $\text{Cu}_3\text{P}/\text{TiO}_2/\text{NC}$  with mesoporous structure can construct an available three-phase interface and exposes a high density of active sites, which was advantageous for electron/mass transport and accelerate the reaction kinetics. As a consequence,  $\text{Cu}_3\text{P}/\text{TiO}_2/\text{NC}$  was adopted as the cathode catalyst for ZAB. The peak power density could reach  $182.9 \text{ mW cm}^{-2}$  as well as superior stability with no distinct current decay after continuous charge-discharge for 220 h, outperforming to  $\text{Pt}/\text{C} + \text{RuO}_2$ . The above results confirmed that  $\text{Cu}_3\text{P}/\text{TiO}_2/\text{NC}$  possesses promising applications in metal-air batteries.

### CRediT authorship contribution statement

**Man Guo:** Methodology, Writing - original draft. **Zhiyang Huang:** Investigation and methodology. **Yuan Qu:** Data curation. **Lixia Wang:** Investigation. **Huatong Li:** Data curation, Methodology. **Tayirjan Taylor Isimjan:** Writing-review & editing. **Xiulin Yang:** Supervision, Writing-review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

The data that has been used is confidential.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2022.121991](https://doi.org/10.1016/j.apcatb.2022.121991).

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